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PATENT SPECIFICATION

NO DRAWINGS

L108,584

1,108,584



Date of Application and filing Complete Specification: 27 July, 1965.

No. 31955/65.

Application made in United States of America (No. 387234) on 3 Aug., 1964.

Complete Specification Published: 3 April, 1968.

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PATENTS ACT, 1949

SPECIFICATION NO. 1,108,584

In accordance with the Decision of the Principal Examiner, acting for the Comptroller-General, dated 6th March 1969, this Specification has been amended under Section 14 in the following manner:-

Page 1, after line 41, insert

"Purification of crude phenol has been proposed by condensation of the impurities contained therein with the requisite proportion of the phenol proposed in British Specification 865,677 there is a disclosure of a process for the purification of phenol derived from cumene and containing colour forming impurities including aliphatic alpha-hydroxy carbonyl compounds which comprise subjecting the impure phenol at an elevated temperature to conditions which cause the substantially complete condensation of the aliphatic alpha-hydroxy carbonyl compounds with phenol to form benzofurans, and separating the phenol substantially completely from the benzofurans. It is stated in that specification that the process may be carried out in the absence of any catalytic agent or in the presence of a catalytically active material such as activated alumina, aluminium silicates, such as acid or alkali-treated pumice and porcelain; acidic or basic ion-exchange resins; mineral acids such as sulphuric acid, phosphoric acid especially in the presence of iron; strong organic acids, as p-toluene sulphonic acid; and surface-active earths such as montmorillonite also known as Fullers' Earth, bentonite, Florida Earth, and attapulgite. The conditions which cause the conversion of aliphatic alpha-hydroxy carbonyl compounds to substituted benzofurans normally also result in the formation of condensation products of compounds such as hydroxy acetone and acetoin, as well as compounds such as diacetyl and mesityl oxide."

THE PATENT OFFICE,
13th May 1969

D 11:

formed during the oxidation, cleavage, and phenol separation sequence. The impurities remaining in the phenol fraction comprise carbonyl compounds, principally the acetone condensation product mesityl oxide which is practically inseparable from the phenol by simple distillation methods. The carbonyl compounds are detrimental in even small amounts because they have color-forming tendencies which render the phenol product unacceptable for many commercial applications.

It is an object of this invention to substantially eliminate the impurities comprising carbonyl compounds from a reaction mixture re-

for the purification of a phenol which has been prepared by the steps of partial oxidation of a secondary alkyl aromatic hydrocarbon to form an alpha hydroperoxy derivative thereof, acid-catalyzed cleavage of said derivative to form a phenol and an aliphatic ketone, neutralization of the cleavage reaction mixture, and separation from the neutralized reaction mixture of a fraction containing the phenol and impurities comprising carbonyl compounds, characterized in that at least a portion of the impurities comprising carbonyl compounds are separated from the phenol fraction by heating said phenol fraction in

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Index at acceptance: —C2 C(3A13B2A1, 3A13B2E, 3A13B2F3)

Int. Cl.: —C 07 c 39/00

COMPLETE SPECIFICATION

Process for the Purification of Phenols

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to the purification of a phenol produced by the acid-catalyzed cleavage of the hydroperoxide resulting from the oxidation of a secondary alkyl aromatic hydrocarbon, and particularly to the purification of phenol produced by cleavage of the hydroperoxide resulting from the oxidation of cumene.

Phenol is prepared by the partial oxidation of cumene to cumene hydroperoxide followed by acid catalyzed cleavage of the hydroperoxide to form a cleavage reaction mixture containing phenol, acetone and unreacted cumene. The cleavage reaction mixture is neutralized and thereafter fractionated to separate the phenol product from the higher and lower boiling constituents of the cleavage reaction mixture. Even with an efficient fractionation column the phenol fraction contains small but detrimental amounts of impurities formed during the oxidation, cleavage, and phenol separation sequence. The impurities remaining in the phenol fraction comprise carbonyl compounds, principally the acetone condensation product mesityl oxide which is practically inseparable from the phenol by simple distillation methods. The carbonyl compounds are detrimental in even small amounts because they have color-forming tendencies which render the phenol product unacceptable for many commercial applications.

It is an object of this invention to substantially eliminate the impurities comprising carbonyl compounds from a reaction mixture re-

sulting from the acid cleavage of the hydroperoxide resulting from the oxidation of a secondary alkyl aromatic hydrocarbon, particularly cumene.

The production of phenol by the partial oxidation of cumene to cumene hydroperoxide and subsequent acid cleavage of the hydroperoxide to phenol and acetone is well known to the art. The process has been applied to the production of phenols in general wherein a secondary alkyl aromatic hydrocarbon corresponding to the desired phenol is oxidized to the hydroperoxide which is subsequently cleaved to form the desired phenol and an aliphatic ketone. While the present description is directed principally to the purification of the phenol fraction recovered from a reaction mixture resulting from the acid cleavage of the hydroperoxide resulting from the oxidation of cumene, the process may also be utilized to eliminate impurities comprising carbonyl compounds from a phenol fraction recovered from a reaction mixture resulting from the acid cleavage of the hydroperoxide resulting from the oxidation of a secondary alkyl aromatic hydrocarbon, for example, *o*-isopropyltoluene, *m*-isopropyltoluene, *p*-isopropyltoluene, *p*-diisopropylbenzene, *sec*-butylbenzene and β -isopropylnaphthalene.

The present invention relates to a process for the purification of a phenol which has been prepared by the steps of partial oxidation of a secondary alkyl aromatic hydrocarbon to form an alpha hydroperoxy derivative thereof, acid-catalyzed cleavage of said derivative to form a phenol and an aliphatic ketone, neutralization of the cleavage reaction mixture, and separation from the neutralized reaction mixture of a fraction containing the phenol and impurities comprising carbonyl compounds, characterized in that at least a portion of the impurities comprising carbonyl compounds are separated from the phenol fraction by heating said phenol fraction in

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admixture with H_2O in contact with a strongly acidic cation exchange resin containing free phosphoric, phosphonic, sulfuric or sulfonic acid groups, thereby converting said carbonyl compounds to compounds having lower boiling points, and separating the lower boiling compounds from the phenol.

Other objects and embodiments of this invention will become apparent in the following detailed specification.

In accordance with the present process, the phenol fraction recovered from the cleavage reaction mixture is heated together with water or steam in contact with a cation exchange resin. The water or steam may be combined with the phenol prior to heating in contact with the resin. The phenol should be heated together with at least from 0.1 to 20 wt. % water or steam at a temperature of from 75°C. to 200°C., preferably from 85°C. to 150°C., in contact with the resin. The optimum contact time is, of course, determined by the particular temperature employed. A contact time equivalent to a liquid hourly space velocity of from 0.1 to 5.0, and preferably from 0.1 to 2.0, is suitable. Although it is not essential to the teaching of the present invention, it may be desirable in order to pre-swell the cation exchange resin to soak it with the phenol water mixture before using it in the reaction.

The cation exchange resins are preferably those of relatively high surface area, for example, those based on matrices which are phenol-formaldehyde condensates, or resinous copolymers of styrene and polyvinylidene monomers such as divinylbenzene and trivinylbenzene, or copolymers of styrene and polyvinyl ethers of polyhydric alcohols such as divinxyethane and trivinxypropane. The resins may be prepared by any of the well-known methods, for example, by heating styrene, or other suitable monoethylenically unsaturated monomer, with divinylbenzene, or other suitable polyvinylidene monomer, at an elevated temperature, for example 100°C., for a suitable period, for example 10 days. However, it is generally preferred to include a catalytic amount of benzoyl peroxide, ammonium persulfate, potassium persulfate, sodium perchlorate, sodium perborate, or other suitable catalyst in the reaction mixture.

The cation exchange resins operable in accordance with the process of this invention are the strongly acidic cation exchange resins containing free phosphoric, phosphonic, sulfuric or sulfonic acid groups, preferably the latter. Sulfonation, or equivalent acid treatment, can be applied either to a monomer, such as styrene, which is subsequently copolymerized with a suitable monomer or, preferably, the copolymer may be formed first and sulfonation, or equivalent acid treatment, effected thereafter.

Particularly preferred are the high surface

area sulfonic acid cation exchange resins characterized by a macro-reticular pore structure such as are described in United Patent Specification No. 956,357. These preferred resins are prepared by copolymerization of a monoethylenically unsaturated monomer, such as styrene, with a polyvinylidene monomer, such as divinylbenzene, in the presence of a common solvent which is further characterized in that it acts as a precipitant with respect to the copolymer product. Any liquids which are solvents for the monomer mixture, which give negligible swelling of the copolymer, which are chemically inert at polymerization conditions and which are substantially insoluble in the suspending medium, when one is employed, are suitable. In the preparation of a styrene-divinylbenzene copolymer, alkanols such as *n*-butyl alcohol, *sec*-butyl alcohol, *t*-amyl alcohol, *n*-hexyl alcohol and decyl alcohol, and also higher saturated aliphatic hydrocarbons such as heptane and iso-octane, are satisfactory.

The cation exchange resin is preferably the nuclear sulfonic acid type. These resins can be prepared, for example, by sulfonating the resin using an excess of concentrated acid, oleum, sulfur trioxide in nitrobenzene, or chlorosulfonic acid as a sulfonating agent.

By the process herein described, the impurities comprising carbonyl compounds are converted to lower boiling materials which are readily separable from the phenol. It is desirable to separate these lower boiling materials substantially immediately as formed to obviate condensation thereof to higher boiling materials. One preferred method comprises utilization of an inert stripping gas such as nitrogen whereby the phenol-water charge stock is continuously passed through the resin bed together with a stream of nitrogen which strips the lower boiling materials from the phenol as they are formed. Another preferred method comprises passing the phenol-water charge in contact with the resin at a reduced pressure, for example, from 100 mm to 400 mm Hg, such that the lower boiling materials are flashed from the phenol as they are formed. Other impurities are incidentally separated pursuant to the present process. For example, in the separation of excess water from the phenol by distillation methods, methylbenzofuran, generally present in at least trace amounts, is recovered as a portion of the steam distillate.

The following examples are presented to illustrate the process of this invention.

EXAMPLE I

Phenol, fractionally distilled from a neutralized cumene hydroperoxide cleavage reaction mixture, was analyzed by gas-liquid chromatography methods and found to contain 0.16 wt. % mesityl oxide. A phenol-water charge stock was prepared by treating said phenol

with steam so as to contain about 5 wt. % water. Approximately 200 cubic centimeters (114 grams) of an acidic cation exchange resin having the trade name Amberlyst 15, which is a sulfonic acid cation exchange resin of macro-reticular pore structure with an average pore diameter of 200—600Å and a surface area of 40—50 square meters per gram, was soaked in the phenol-water charge stock for a 1 hour period in order to pre-swell the resin. The pre-swelled resin was placed in a fixed bed in a vertical tubular reactor, and the phenol-water charge stock was charged therethrough at a liquid hourly space velocity of 0.5, the charge being in an upflow direction. The reactor was maintained at about atmospheric pressure and at a temperature of 95°C. The reactor effluent was collected and analyzed by gas-liquid chromatography and found to contain less than .03 wt. % mesityl oxide.

EXAMPLE II

Phenol, fractionally distilled from a neutralized cumene hydroperoxide cleavage reaction mixture and containing .16 wt. % mesityl oxide, was treated with steam so as to contain about 5 wt. % water. Approximately 200 cc of the sulfonic acid cation exchange resin described in Example I was pre-swelled in the phenol-water charge stock for a 1 hour period. The resin was disposed in a fixed bed in a vertical tubular reactor. The phenol-water charge stock was thereafter processed upflow through the resin bed at a liquid hourly space velocity of 0.5 together with dry nitrogen stripping gas charged at a rate of about 214 liters per liter of charge stock, the reactor being maintained at atmospheric pressure and at a temperature of about 95°C. The reactor effluent was collected and analyzed by gas-liquid chromatography and found to contain less than .0075 wt. % mesityl oxide.

EXAMPLE III

Phenol, fractionally distilled from a neutralized cumene hydroperoxide cleavage reaction mixture and containing .18 wt. % mesityl oxide, was treated with steam so as to contain about 5 wt. % water. Approximately 200 cc of the sulfonic acid cation exchange resin described in Example I was soaked in a phenol-water charge stock for a 1 hour period in order to pre-swell the resin. The resin was disposed in a fixed bed of a vertical tubular reactor. The phenol-water charge stock was thereafter charged upflow through the resin bed at a liquid hourly space velocity of 0.5. The reactor was maintained at a reduced pressure of about 200 mm and at a temperature of 100°C. The reactor effluent was continuously withdrawn and analyzed by gas-liquid chromatography methods and found to contain less than .0051 wt. % mesityl oxide.

WHAT WE CLAIM IS:—

1. A process for the purification of a phenol which has been prepared by the steps of partial oxidation of a secondary alkyl aromatic hydrocarbon to form an alpha hydroperoxy derivative thereof, acid-catalyzed cleavage of said derivative to form a phenol and an aliphatic ketone, neutralization of the cleavage reaction mixture, and separation from the neutralized reaction mixture of a fraction containing the phenol and impurities comprising carbonyl compounds, characterized in that at least a portion of the impurities comprising carbonyl compounds are separated from the phenol fraction by heating said phenol fraction in admixture with H₂O in contact with a strongly acidic cation exchange resin containing free phosphoric, phosphonic, sulfuric or sulfonic acid groups, thereby converting said carbonyl compounds to compounds having lower boiling points, and separating the lower boiling compounds from the phenol.
2. Process as claimed in claim 1, characterized in that the phenol fraction admixed with H₂O is contacted with a sulfonic acid cation exchange resin.
3. Process as claimed in one of the claims 1 and 2, characterized in that the phenol fraction to be purified has been recovered from the reaction mixture resulting from the acid cleavage of the hydroperoxide produced by the oxidation of cumene.
4. Process as claimed in one of the claims 1 to 3, characterized in that the phenol fraction to be purified is admixed with from 0.1 to 20 wt. % H₂O and contacted with a sulfonic acid cation exchange resin at a temperature of from 75° to 200°C.
5. Process as claimed in one of the claims 1 to 4, characterized in that the phenol fraction to be purified is admixed with H₂O and is passed into contact with a macro-reticular sulfonic acid cation exchange resin at a liquid hourly space velocity within the range of from 0.1 to 5.0.
6. Process as claimed in one of the claims 1 to 5, characterized in that the phenol fraction to be purified in admixture with H₂O is contacted with the cation exchange resin at a reduced pressure of from 100 mm to 400 mm Hg and the lower boiling compounds produced therefrom are flashed from the phenol fraction.
7. Process as claimed in one of the claims 1 to 5, characterized in that an inert gas stream is passed with the phenol-H₂O mixture into contact with the cation exchange resin and is used to strip the lower boiling compounds from the phenol as they are formed.
8. Process as claimed in one of the claims

1 to 7, characterized in that the cation exchange resin is pre-swelled prior to its use in the reaction by soaking it in a portion of the phenol fraction-H₂O mixture.

5 9. Process for the purification of a phenol prepared from a secondary alkyl aromatic hydrocarbon, substantially as described.

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Agents for the Applicants.

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